RECYCLING OF FIRE CLAY WASTE MATERIAL IN TRIAXIAL COMPOSITION

A thesis submitted

By

JOGESWAR GUIYA

109cr0111

(Under the guidance of Prof. S. Bhattacharyya)

In the partial fulfillment of the requirements of degree
Of
Bachelor of Technology

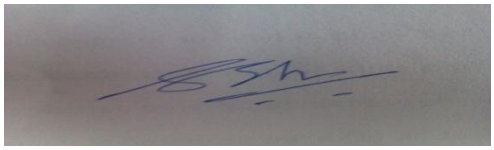
DEPARTMENT OF CERAMIC ENGINEERING
NATIONAL INSTITUTE OF TECHNOLOGY
ROURKELA

NATIONAL INSTITUTE OF TECHNOLOGY
ROURKELA

CERTIFICATE

This is to certify that the thesis entitled, "**RECYCLING OF FIRE CLAY WASTE MATERIAL IN TRIAXIAL COMPOSITION**", submitted by **Mr. JOGESWAR GUIYA (Roll no. 109CR0111)** in partial fulfillment of the requirements of the award of Bachelor of Technology Degree in Ceramic Engineering at the National Institute of Technology, Rourkela is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other university / institute for the award of any Degree or Diploma.



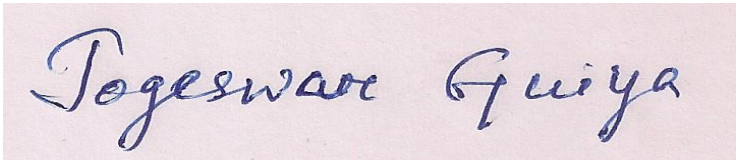
Prof. Sunipa Bhattacharyya
Department Of Ceramic Engineering
National Institute of technology
Rourkela-769008

Date: 10.05.2013

ACKNOWLEDGEMENT

With deep respect, I avail this opportunity to express my gratitude to **Prof. Sunipa Bhattacharyya** Department of Ceramic Engineering, National Institute of Technology, Rourkela for her inspiration and guidance and valuable suggestion throughout this research work. Her vast knowledge in the field of Science and Technology helped to enlighten me. It would have been impossible on my part to come out with this project report without her. I would like to thanks to the HOD, Ceramic Department and all other faculties for their support and valuable suggestions throughout this research project. I would also take this opportunity to express my gratitude to the non-teaching staff for their help and kind support at various stages of work.

I am also thankful to the Research Scholar in the Department of Ceramic Engineering for helping out in labs and analysis. And lastly I am thankful to my parents and friends for their constant support.



Jogeswar guiya

109CR0111

Abstract

The quartz is partially and fully replaced by the fire clay waste material (a waste of Indian steel plant) in the range of 0%, 50% and 100% in a traditional triaxial composition having clay, quartz and feldspar. The effects of this substitution upon firing in the temperature range of 1150-1250^{o}C were investigated by measuring the linear shrinkage, apparent porosity, bulk density and strength. The results showed that the waste material containing samples achieved better properties in the entire temperature range of firing.

Table contents page

List of table and figure

Chapter 1

Introduction

1.1 introductions

Triaxial porcelain is one of the most widely studied ceramic systems. Composed primarily of clay–quartz– feldspar, it has got diverse applications like whiteware, stoneware, insulators, etc. In a porcelain composition, clay provides plasticity and green strength during forming stage, and contributes to mullite formation after firing. Quartz acts as filler material whose coarse grains provide resistance to cracking during drying and form skeletal network during firing to reduce pyroplastic deformation. Fluxing action of feldspar above 1000^{o}C leads to densification in the presence of a reactive liquid phase that partly dissolves quartz and clay which leads to formation of interlocked acicular mullite crystals embedded in feldspathic glass.

It is said that the quartz is the bone of the body, feldspar act as a blood of the body and clay flesh of the body. Feldspar melt first starts taking quartz into solution and helps in conversion. During the firing of triaxial composition only small amount of quartz get dissolved and rest remains unreacted, these are called free quartz this free quartz undergoes phase transformation which leads to development of stresses and adversely affect the mechanical properties of the triaxial composition. To improve the mechanical properties various attempts were made to substitute quartz with other material like alumina, alumina-silicate etc.

The naturally occurring raw materials are depleting fast in India and in other countries. But with the growth of the industry they consume a huge amount of naturally occurring raw material and produces large amount of waste. The utilization of these waste materials may solve some of the problem related to storage of waste material. To take advantage of this opportunity, wastes must be regarded as possible raw materials and should be carefully characterized in order to predict their behaviour during processing and their effects on the final products. The use of industrial

wastes as alternative raw materials can be considered viable only if the manufacturing process remains essentially unchanged and the quality and characteristics of the product are not unduly affected

Since fire clay waste material is fired product containing quartz and mullite phases, it has very low shrinkage, which is an essential criterion for a filler material in porcelain composition so here attempt is made to study the changes in fired properties of triaxial ceramic through fully and partially substituting quartz by used fire clay waste material.

Chapter-2

Literature review

Previous work:

Kausik dana(1) et al. have worked on the subject, Effect of substitution of fly ash for quartz in triaxial kaolin–quartz–feldspar system. They substituted the quartz by 5, 10 and 15 wt% of fly ash. The firing temperature was in the range of 1150-1300 ^{o}C. The effects of this substitution upon firing at different temperature were investigated by measuring the linear shrinkage, bulk density, apparent porosity and flexural strength. The bulk density and apparent porosity was measured by water displacement method of Archimedes principle. Flexural strength was measured by 3-point bending method. The quantity of residual quartz and mullite content is estimated by quantitative XRD analysis. Microstructure was studied by the SEM. The results showed that fly ash containing samples achieved higher densification and flexural strength in the temperature range of 1150-1300 ^{o}C than the traditional porcelain body. From the investigation it concluded that Substitution of quartz by fly ash in a normal porcelain body increases the linear shrinkage, Bulk density and decreases the apparent porosity in the entire temperature range of 1150–1300 °C. This may be due to the formation of low viscosity of glass which flows easily and helps in liquid phase sintering. The mullite content increases with the addition of fly ash in place of quartz and as a result the flexural strength improves significantly. Expectedly, residual quartz content decreases with fly ash addition.

Emilia (2) et al. have worked on the subject 'Ceramics from blast furnace slag, kaolin and quartz'. They have studied three new ceramic batches with zero feldspar and 30, 50 and 70 wt.% of blast furnace slag. The thermal behavior of raw materials is studied by the TG-DTA. The structure of final material and their phase were studied by SEM and X-ray Diffraction. After sintering, the densified samples were evaluated measuring linear shrinkage, water absorption and mechanical properties. It revealed that good densification of sample comes at sintering interval

of 1200-1220^{o}C due to the formation of pyroxene and anorthite solid solution. The new materials show high crystalline nature. It concluded that new low-cost ceramics, with no traditional fluxes and 30, 50 and 70% blast furnace slag were synthesized at sintering temperatures of 1200–1220 ◦C. The obtained samples have good mechanical properties.

Swapan Kumar Das (3) et.al has worked on the subject of 'Partial substitution of feldspar by B.F. slag in triaxial porcelain- Phase and microstructural evolution'. They partially substituted Feldspar by B.F. slag to the extent of 5–20 mass% in a triaxial porcelain composition consisting of 45 mass% kaolinitic clay, 30 mass% feldspar, 25 mass% quartz. The compact green body was fired at the temperature of 1200 ^{o}C for soaking time 120 minute. The fired samples were subjected to physical test such as linear shrinkage, bulk density, apparent porosity and flexural strength. The results revealed that partial substitution of feldspar by blast furnace slag in a normal porcelain composition enhances the densification and strength. Mullite crystals present in normal porcelain body gradually reduced with increase in slag content and remains almost unchanged beyond 10% slag addition. Quartz level also reduced upto 5% slag addition beyond which remains unchanged. Distinct changes in microstructure also show gradual disappearance of needle shaped mullite crystals and reduction of quartz grains to a certain level. Microstructures of slag-containing bodies showed the appearance of anorthite formed by crystallization of the melted glassy phase.

T.K Mukhopadhyay et.al (4) have worked on the subject of 'Effect of fly ash on the physico-chemical and mechanical properties of a porcelain composition'. In a traditional triaxial porcelain composition quartz was fully substituted by fly ash. The firing temperature is in the range of 1100-1300◦c. The effect of this substitution and subsequently firing the specimens at different temperatures (1100–1300◦C) were investigated by measuring related properties. The

fired specimens were subjected to physical test such as linear shrinkage, apparent porosity, bulk density, flexural strength. Apparent porosity and bulk density were measured by water displacement method according to Archimedes principle and flexural strength was determined by 3-point bending method. Phase changes and microstructure evolution was determined by SEM and XRD technique. Optimum properties were obtained with the specimen having 30% fly ash. Requirement of feldspar was found to be reduced to 20%. The flexural strength of the porcelain body reached a maximum at 1300^{o}C while the apparent porosity value reached almost zero. There was around 20% increase in flexural strength in comparison to that of the conventional triaxial body. Mullite content was found to increase with increasing proportion of fly ash. SEM studies revealed the presence of a-quartz and secondary mullite needles embedded in a glassy matrix. Extensive cracking around the quartz grains was also observed. Intense interlocking of fine mullite needles were found to be responsible for development of higher flexural strength in fly ash incorporated porcelain body.

M.K Haldar et.al(5) have work in the subject of ' Effect of substitution of sand stone dust for quartz and clay in triaxial porcelain composition'. They partially substituted Quartz and kaolin by sand stone dust. In traditional triaxial porcelain composition consists of kaolin, quartz and feldspar. The effect of substitution upon heating at different temperatures 1050–1150 ℃ were studied by measuring the linear shrinkage, bulk density, porosity and flexural strength. Qualitative phase and micro structural analysis on selected samples were carried out using XRD and SEM technique. The results showed that the samples of all the batches achieved higher density and almost full vitrification at around 1115^{o}C compared to around 1300^{o}C for traditional triaxial porcelain composition.

Plan of work

(a)Chemical analysis of fire clay waste material

b) XRD of fire clay waste material

c) Batch preparation

d) Batch mixing by pot milling

e)Fabrication by hydraulic pressing

f) Sintering in the temperature range of 1150-1250°c

g) Characterization of sintered sample by

i) Apparent porosity

ii) Bulk density

iii) Linear shrinkage

iv)Cold crushing strength

CHAPTER -3

EXPERIMENT PROCEDURE

3.1 Procedure for the chemical analysis of fire clay waste:

- 0.5178 gm of unknown waste material was taken with sodium carbonate and sodium hydroxide in the platinum crucible and fused in the furnace at a temperature of 1000^{o}C
- The fused mass was taken and it was dissolved in 1:1 HCL and dried overnight.
- Then again 50 ml of 1:1 HCL solution was added to it and filtered through whatman-540 filter paper and filtrate was collected in a 250 ml of volumetric flask. The residue which is kept in the filter paper was washed thoroughly with distilled water. The residue was taken in a pre -weighed crucible and fired at 1000^{o}C. After firing the weight of the crucible was taken. From the difference of the weight silica content calculated.
- 50 ml of filtrate solution was taken in a 250 ml beaker then few drop of methyl red indicator was added. Then ACC buffer solution was added till the colour changed to light yellow. The solution was filtered through whatman-541 filter paper. From the residue mixed oxide estimation done.
- The filtrate was collected in a 250 ml volumetric flask and marked as filtrate 2. This filtrate was used for CaO and MgO estimation.
- For the iron determination 10ml of filtrate-1 was taken in a conical flask , 10 cc of ammonium thiocyanate was added, colour changed to blood red, then this solution was titrated with mercurous nitrate solution.
- For the CaO and MgO estimation, EDTA titration was done. Report of the result is given in table 2

3.2 Batch preparation

Three different porcelain batches were prepared as per the batch composition provided in table 1. The clay, quartz, feldspar and fire clay waste material is used for the batch preparation. The fire clay waste was ground thoroughly, sieved by the 75µm sieve. The entire batch mixed separately and wet ground in the pot mill for 4-6 hr. The obtained homogeneous slurry was dried for 24 hrs in the temperature range of 100-110^{o}C for evaporation of water, the dried mass was powdered to break the agglomerate. Bars of the size 65×30×10 mm were compacted using uniaxial pressing at 4 ton for 90 sec. The shaped samples were dried at 100-110℃.

The dried sample was fired in different temperature of 1150^{o}C, 1200^{o}C and 1250^{o}C for soaking time of 2hrs. The heating rate is 5^{o}C / min and heating rate is maintained during firing in the electrical furnace. The fired samples were then subjected to physical test such as linear shrinkage, apparent porosity, bulk density and cold crushing strength. The conventional liquid displacement method was followed to measure apparent porosity and bulk density according to Archimedes principle and cold crushing strength were measured by hydraulic pressing machine.

Calculation of apparent porosity and bulk density:

Apparent porosity =W-D/(W-S)*100
Bulk density =D/W-S
Where D: Dry weight
S: Suspension weight
W: Soaked weight

Table 1 batch composition

batch	Clay(%)	Quartz(%)	Feldspar(%)	Fire clay waste(%)
B1	45	30	25	……
B2	45	……	25	30
B3	45	15	25	15

CHAPTER-4

Result

And

Discussion

The chemical analysis result of fire clay waste material is given below

Table-2 chemical analysis of the fire clay waste material

	(%)
SiO2	62.688
Al2O3	26.863
Fe2O3	9.541
MgO	1.946
CaO	1.353

The results of chemical analysis of fire clay waste material showed that appreciable amount of ferruginous (Fe_2O_3) and calcareous (CaO + MgO) impurities were present 9.54% and 3.30% respectively.

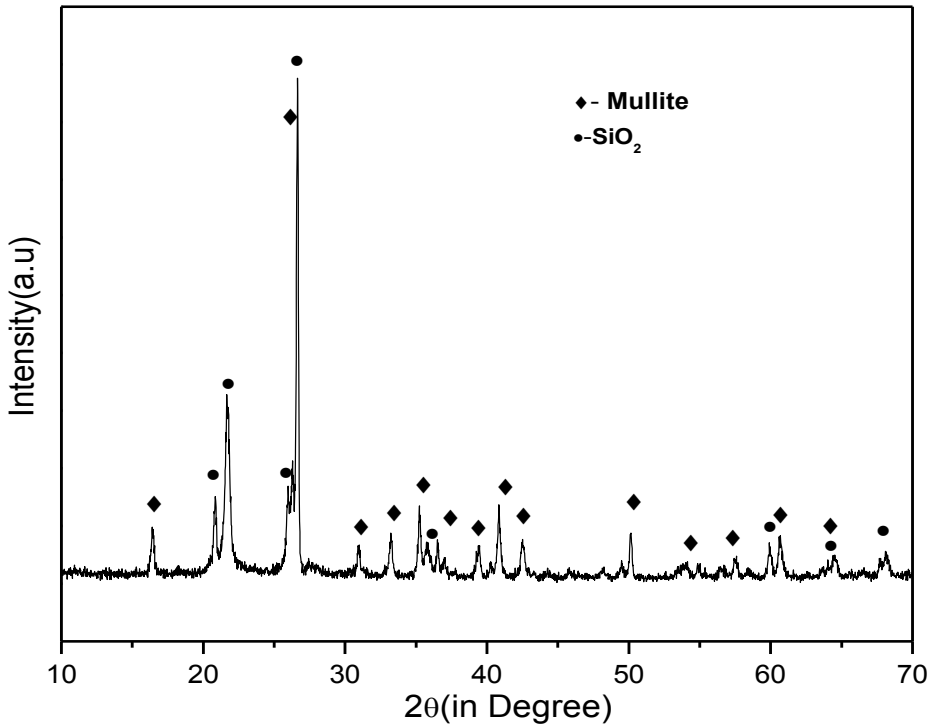


Figure.1 XRD of the fire clay waste material

XRD analysis of fire clay waste material showed the presence of mullite and quartz peak in the sample.

Dimensions of green samples and fired samples are given below

.

Table 3 Dimension of green samples

Sample	Length(mm)	Breadth(mm)	Height(mm)	Weigth(gm)
S1(0%)	65.75	30.69	9.58	31.412
S2 (0%)	65.75	30.65	9.83	31.875
S3(0%)	65.68	30.69	9.76	31.672
S4(0%)	65.63	30.37	9.21	30.05
S5(0%)	65.84	30.55	8.25	27.97
S6(0%)	65.83	30.35	9.24	29.57
S7(15%)	65.75	30.70	8.84	27.990
S8(15%)	65.69	30.69	10.03	31.955
S9(15%)	65.68	30.68	10.63	33.882
S10(15%)	65.63	30.20	8.56	27.76
S11(15%)	65.65	30.43	8.96	29.14
S12(15%)	65.67	30.39	9.89	31.82
S13(30%)	65.75	30.63	8.09	27.953
S14(30%)	65.75	30.60	9.06	29.785
S15(30%)	65.74	30.68	9.46	30.013
S16(30%)	65.64	30.33	10.63	34.30
S17(30%)	65.66	30.39	10.52	33.37
S18(30%)	65.64	30.35	8.32	27.00

Table-4 Dimensions of fired samples at temperature of 1150°c

List of samples	Length(mm)	Breadth(in mm)	Height(in mm)	Weight(gm)
S(0%)	62.09	28.81	9.15	29.47
S(0%)	62.15	28.74	9.25	29.87
S(15%)	61.17	28.68	8.15	26.24
S(15%)	62.04	28.86	9.23	29.94
S(30)	60.81	28.25	8.13	26.17
S(30)	60.64	27.92	8.51	27.87

Table -5 Dimensions of fired samples at temperature of 1200°c

List of samples	Length(mm)	Breadth(mm)	Height(mm)	Weight(gm)
S(0)	60.71	28.15	7.38	24.30
S(0)	61.37	28.44	8.18	27.32
S(15)	60.91	28.20	8.21	27.34
S(15)	60.24	28.45	9.08	29.81
S(30)	60.42	27.93	9.73	31.28
S(30)	60.41	27.99	7.78	25.31

Table-6 Dimension of fired samples at temperature of 1250°c

List of sample	Length(mm)	Breadth(mm)	Height(mm)	Weight(gm)
S(0)	59.05	27.55	8.74	29.61
S(0)	59.19	27.32	8.11	28.06
S(15)	58.12	27.16	9.29	31.65
S(15)	58.78	27.05	7.52	25.95
S(30)	57.59	26.75	8.95	27.97
S(30)	58.57	27.00	9.56	9.56

Calculation of % linear shrinkage:

Table-7 sample-shrinkage

At temperature 1150℃ List of samples	Linear shrinkage (%)
S(0%)	5.51
S(15%)	5.80
S(30%)	7.64
At temperature 1200℃	
S(0%)	7.28
S(15%)	6.99
S(30%)	7.97
At temperature 1250℃	
S(0%)	9.95
S(15%)	10.97
S(30%)	11.58

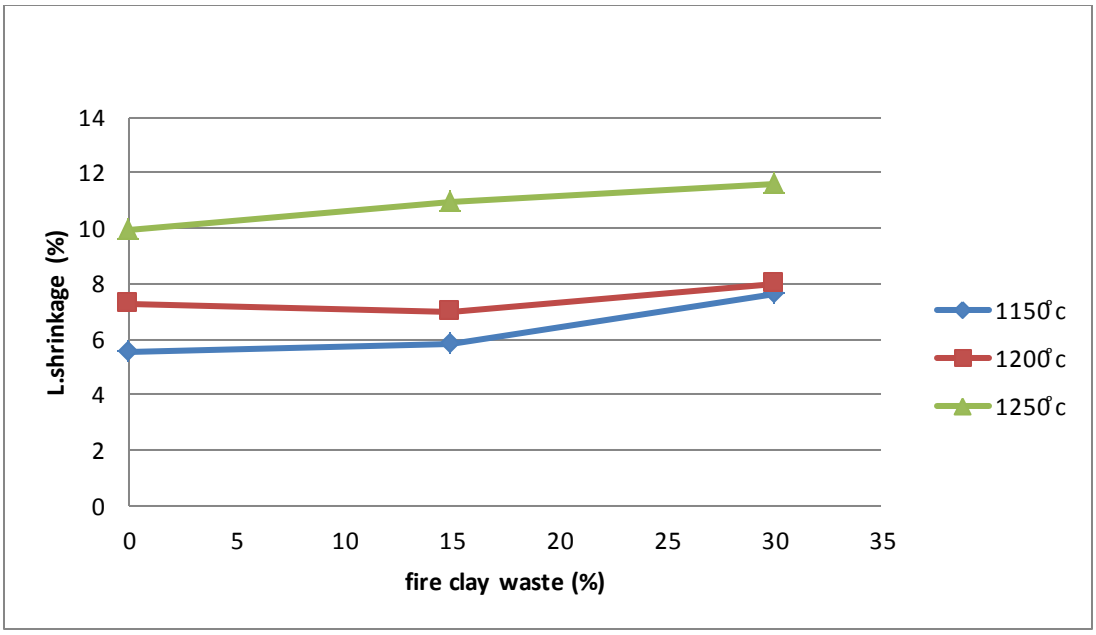


Fig-2 variation in % linear shrinkage with % of waste material added.

The variation of % linear shrinkage with the amount of waste material added was plotted in fig-2. From the figure it was found that for the entire porcelain composition % linear shrinkage increases with increasing firing temperature. Substitution of fire clay waste material in place of quartz also increased the shrinkage value in the entire firing range. This may be due to the presence of fluxing alkaline earth in fire clay waste material, which enter into the glassy phase and reduces the viscosity and resulting comparatively higher shrinkage.

Table-8. Dry weight, soaked weight and suspended weight of the samples:

At temperature 1150˚c	Dry weigth(D)	Suspended weight(s)	Soaked weight(w)
S(0%)	4.1725	2.590	4.675
S(15%)	4.2777	2.646	4.950
S(30%)	8.7333	5.396	9.80
At temperature 1200˚c			
S(0%)	6.8061	4.196	7.846
S(15%)	5.6516	3.484	6.377
S(30%)	5.2340	3.243	5.842
At temperature 1250˚c			
S(0%)	10.4523	6.298	11.052
S(15%)	7.4927	4.516	7.824
S(30%)	6.1554	3.709	6.354

Table-9 Calculated apparent porosity

At temperature 1150˚c List of samples	Apparent porosity (%)
S(0%)	24.10
S(15%)	29.179
S(30%)	24.340
At temperature 1200˚c	
S(0%)	28.491
S(15%)	25.05
S(30%)	23.30
At temperature 1250˚c	
S(0%)	12.61
S(15%)	10.01
S(30%)	7.509

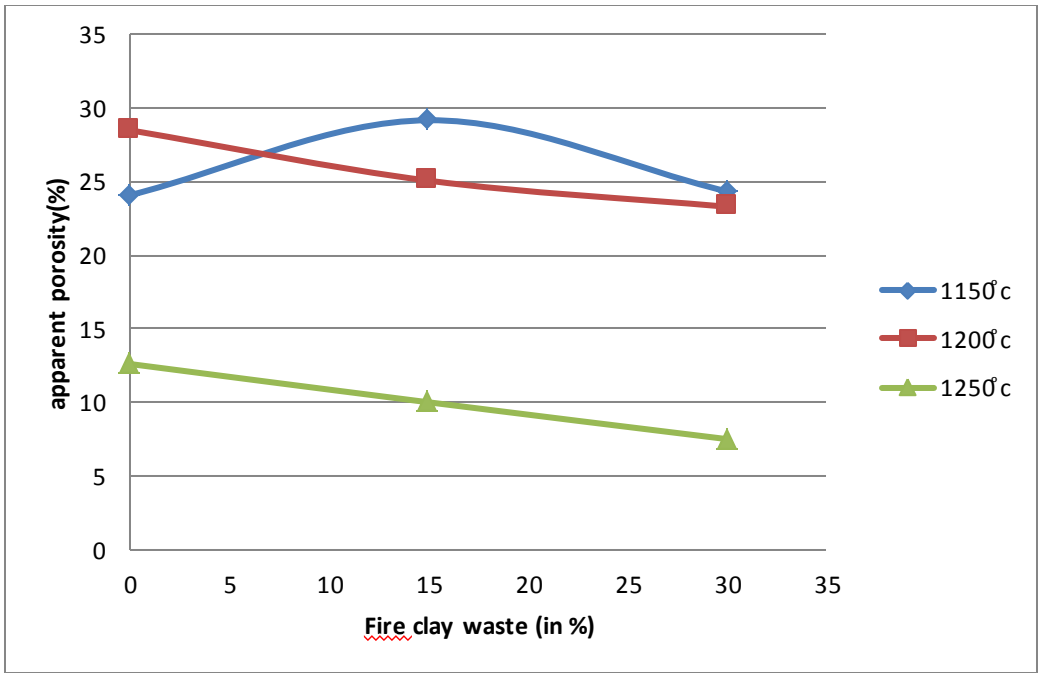


Fig-3 Variation of % apparent porosity with amount of waste material added.

The % apparent porosity was found to decrease with increasing amount of waste material added at 1200^{o}C and 1250^{o}C. Waste material containing samples matured early than normal porcelain batch. 30% waste containing sample exhibit minimum porosity at 1250^{o}C. This is due to the formation of low viscosity glass in presence of other oxide coming from fire clay waste which flows easily to fill up the pores. It is expected if firing temperature increased up to 1300^{o}C then porosity may decreased to negligible range.

Table-10 Calculated bulk density

At temperature 1150˚c List of samples	Bulk density(gm/cm3)
S(0%)	2.00
S(15%)	1.85
S(30%)	1.97
At temperature 1200˚c	
S(0%)	1.864
S(15%)	1.953
S(30%)	2.013
At temperature 1250˚c	
S(0%)	2.198
S(15%)	2.26
S(30%)	2.32

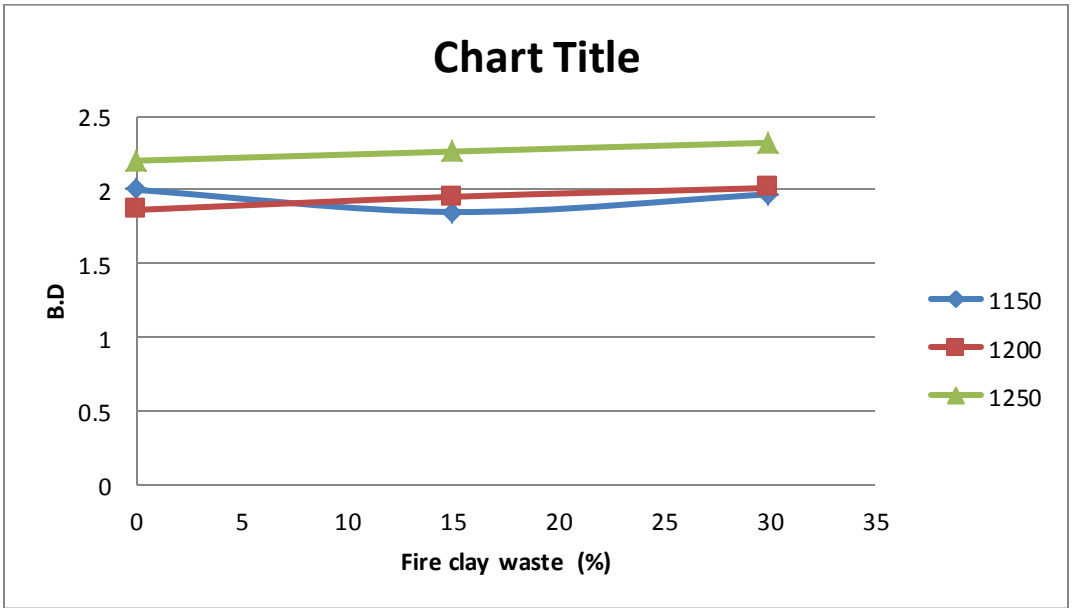


Fig-4 Variation of bulk density with the amount of waste material added.

From the figure it was found that there was an increasing trend in bulk density with increasing the amount of fire clay waste added and with increasing the firing temperature. This is due to the increased consolidation at higher temperature. Waste containing batches exhibit higher B.D value through firing temperature ranges due to higher amount of alumna present in those batches and also due to the formation of less viscous glass which helps in consolidation process.

Table-11 CCS

At temperature 1150˚c List of samples	CCS(kg/cm2)
S(0%)	8.55
S(15%)	8.06
S(30%)	10.09
At temperature 1200˚c	
S(0%)	8.35
S(15%)	9.50
S(30%)	10.27
At temperature 1250˚c	
S(0%)	11.91
S(15%)	12.92
S(30%)	13.91

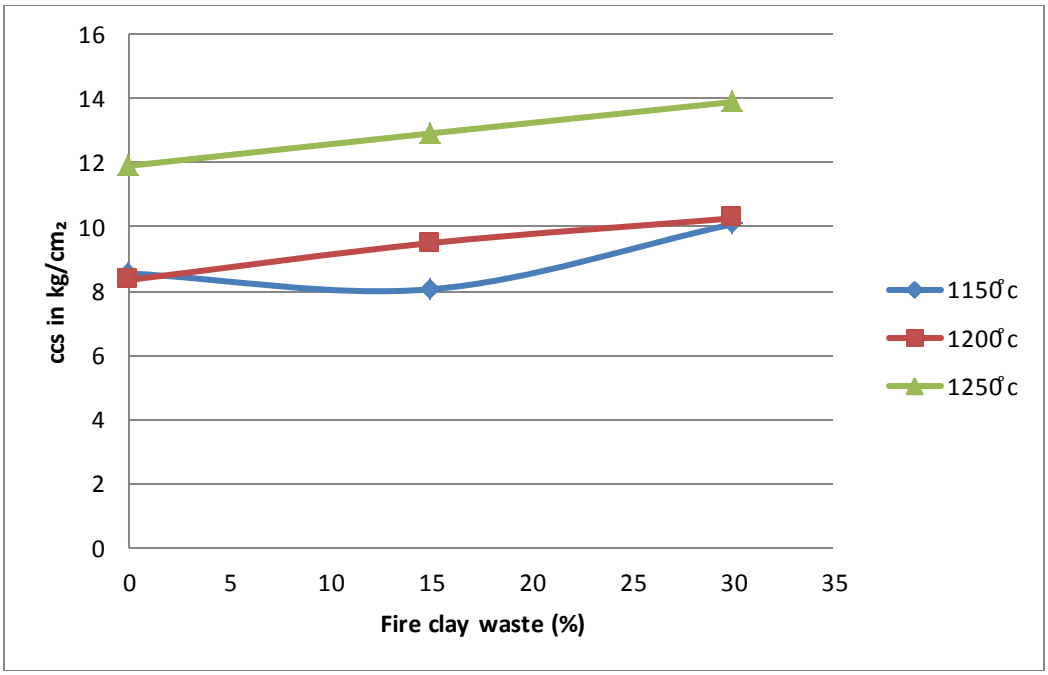


Fig-5 Variation of CCS with amount of fire clay waste added.

From the figure it was found that the CCS value increases as the amount of waste addition increases. This change corresponds well with the changes of apparent porosity and bulk density.

Chapter -5

Conclusion

From the experiment we can conclude that:

Substitution of quartz by fire clay waste material in tri-axial composition increases shrinkage and bulk density (2.32g/cm3) whereas decreases the apparent porosity in the entire temperature range of firing. This may be due to the formation of low viscosity glass which flows easily and assist in liquid phase sintering.

Chapter 6

References

1. kausik dana, sukhen das, swapan kumar das .'Effect of substitution of fly ash for quartz in triaxial koalin-quartz-feldspar system'. J. Eur. Ceram. Soc., 24 (2004) 3169–3175

2. Emilia ,karamanova, george avdeev .Ceramics from blast furnace slag ,koalin and quartz. J. Eur. Ceram. Soc. 31 (2011) 989–998

3.Kausik dana ,Swapan kumar Das .Partial substitution of feldspar by b.f slag in triaxial porcelain :phase and microstructure evolution. Journal of the European Ceramic Society 24 (2004) 3833–3839

4.T.K. Mukhopadhyay , S. Ghosh, J. Ghosh, S. Ghatak, H.S. Maiti .Effect of fly ash on the physico-chemical and mechanical properties of a porcelain composition. Ceramics International 36 (2010) 1055–1062

5.M.K haldhar,S.K das .The Effect of substitution of sandstone dust for quartz and clay in triaxial porcelain composition. Bull. Mater. Sci., Vol. 35, No. 5, October 2012, pp. 897–904. © Indian Academy of Sciences.